

## **Short Term Innovative Research Program: Nanoengineered Reactive Materials for Tunable Ignition and Energy Release**

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### **I. Background**

Most conventional explosives can be roughly categorized into two classes – molecular materials and intermolecular composites. Molecular materials refer to species such as the nitroalkanes (e.g. nitromethane) and cyclic nitramines (e.g. TNAZ, RDX, HMX) that release chemical energy primarily by converting singly bonded nitrogen to more stable doubly and triply bonded forms. Intermolecular composites release chemical energy by anion exchange between the composite phases and the formation of new and more thermodynamically stable compounds.<sup>1</sup> Traditionally, molecular materials have been the premier energetic compounds because they can store relatively large amounts of energy (in the range of 4 kJ/cc), they can be rapidly ignited by mechanical shock to produce high power, the products of reaction are superheated gases that do work on their surroundings, and they can be mass produced. In contrast, intermolecular composites (typified by one of the oldest energetic materials: black powder) store substantially more chemical energy, up to 25 kJ/cc, but the ignition mechanisms are most commonly thermal.<sup>2</sup> Consequently, the energy release is regulated by diffusion, and although their reactions can produce temperatures in excess of 2000°C, the relatively slow resulting kinetics dramatically limits power output.

An alternative to conventional explosives that has been gaining increasing interest have been termed reactive materials, and are defined as systems in which two or more non-explosive solid phases combine to ignite and release chemical energy. An example that has been used for many years for welding and as a pyrotechnic initiator is thermites where Al powder is combined with a metal oxide. More recently, researchers have begun examining self-propagating reactions in reactive materials with nanometer-scale features to explore whether energy storage and power output can be enhanced to the point that these materials can be used in conjunction with (or even replace) traditional explosives.<sup>3,4</sup> It has been reported, for example, that by reducing diffusion distances by engineering the structural dimensions to the nanometer scale, reaction propagation front speeds in reactive materials can be increased by orders of magnitude compared to similar systems with micron-scale features. This result has been confirmed by recent molecular simulations of the shock initiation of Ni/Al nanolaminates, where propagation speeds of 200 m/s were determined.<sup>4</sup> It was also determined from the simulations that nanopores can increase the energy release rate due to mechanical intermixing caused by pore collapse, and that energy release rates are also enhanced by melting of the Al and Ni layers.

Reactive materials were discussed in a report entitled “*Advanced Energetic Materials*” that was released by the National Academy of Sciences in 2004.<sup>5</sup> In this report it was noted that the incorporation of reactive materials into munitions such as shape charges and explosively formed penetrators can significantly enhance the efficacy of these munitions against both hard and soft targets. The report also notes that “reactive materials research and characterization are in an early state of exploration and development” and that “Greater emphasis should be given to materials engineering research...”.

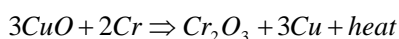
From the limited research that has been done over the last 5 years it appears that nanostructured reactive materials hold promise for storing large quantities of energy in excess of traditional explosives, and that the power output from self-sustaining reactive fronts can be controlled (and greatly enhanced) by manipulating their nanostructure. Furthermore, reactive materials can in principle play a structural role in munitions, leading to an overall increase in net lethality. Clearly, however, much work is needed before these materials can reach their full potential as safe and effective energetic materials with tunable energy density and power output.

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The key to establishing these technology capabilities lies in (1) developing a fundamental understanding of ignition and energy transfer in reactive materials, with particular attention to nanometer length scales, and (2) developing new processes that produce ordered multiphase assemblies that can tune energy content and power output for specific applications. Our research team has brought a combination of expertise in computational materials research and processing science that is ideally suited to accomplish this learning, and establish a vibrant new research direction in energetic materials.

## II. Research Objectives

A short term innovative research effort was carried out. The objectives of which were to (1) use modeling to develop principles for the rational engineering of nanostructured solids as reactive materials with tunable ignition and energy release rates, and (2) experimentally engineer and demonstrate prototype nanostructured CuO/Cr reactive laminates with heat release via the reaction



that are initiated either thermally or electrically via Joule heating.

## III. Approach

Our program used parallel modeling and experimental efforts to explore complementary aspects of the controlled ignition and power output of nanostructured energetic materials. In the modeling effort, multi-scale modeling of the Joule heating and subsequent reaction of Ni/Al nanostructured solids were carried out using specialized multi-scale modeling codes developed in our group that couple continuum heat and current transport with a molecular simulation. Using these codes the rate and mechanism of exothermic mixing of Ni and Al as a function of geometry and applied current was characterized.

In the experimental effort CuO/Cr nano-laminates with varying interlayer thicknesses were engineered using dual source RF-magnetron sputtering. Energy output was initiated via exothermic oxygen transfer reactions within the nano-laminates by both thermal and Joule heating. Pre- and post-ignition TEM characterization and in site X-ray diffraction was used to determine relations between interface structure, extent of reaction and power output, and post-initiation microstructure.

## IV. Major Accomplishments

### IV.i Experimental Effort

Dual source RF-magnetron sputtering was used to engineer CuO/Cr nano-laminates with systematically varied thicknesses. These structures were then characterized using TEM cross sectional imaging. Shown in Figure 1 below are three of these images that were taken from samples created under different deposition conditions. The layers vary in number and in thickness. In all cases the layers have very uniform thicknesses that are separated by atomically resolved interfacial regions. This precise control of the nanostructure allows a detailed, quantifiable comparison between their structure and initiation properties.

Two methods of initiating the exothermic chemistry were used. The first was a controllable conversion via thermal ignition, during which the conversion of the Cr-CuO multi-layers into  $\text{Cr}_2\text{O}_3$  – Cu multilayers was demonstrated. Figure 2 shows *in situ* X-ray diffraction scans as a function of increasing temperature for a nano-laminate with the initial structure 290 nm CuO – 100 nm Cr x 10 as it was heated. The abrupt reduction of Cr (002) and simultaneous appearance of Cu (111) indicate a thermal initiation temperature of ~ 640 °C for a reaction that occurs over several minutes. This data not only establishes the temperature at which the reaction occurs, but also provides data about the final structure that can be contrasted to electrical ignition.

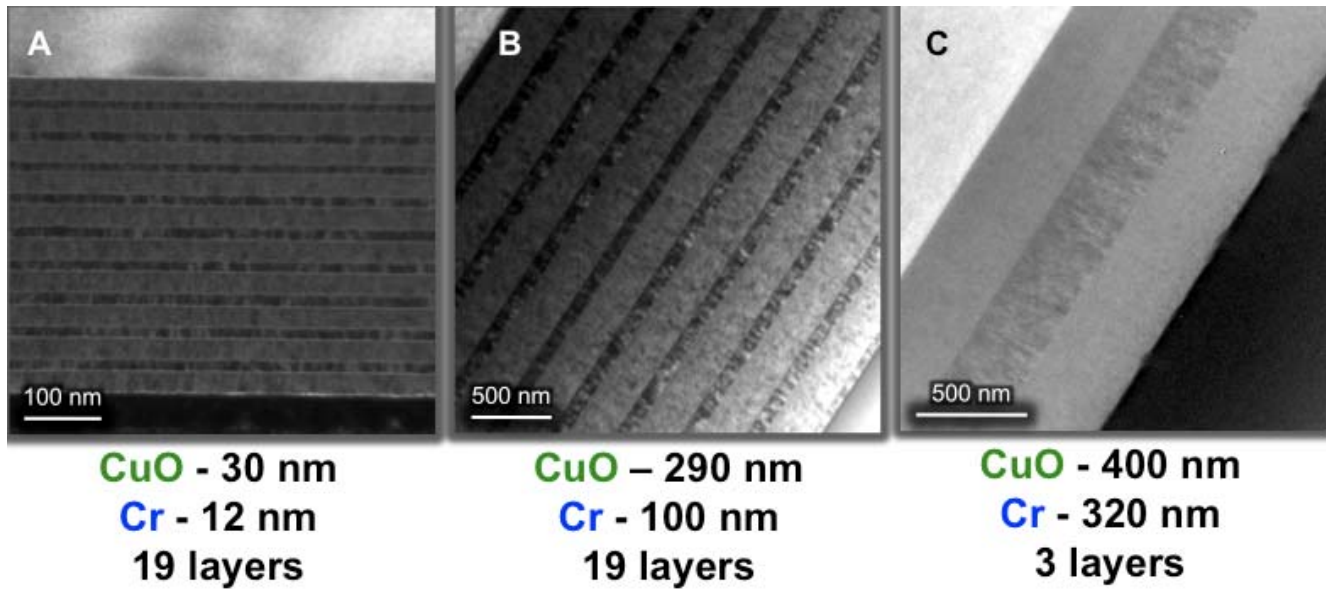


Figure 1: Cross sectional TEM images of several nano-laminates engineered via varying growth conditions.

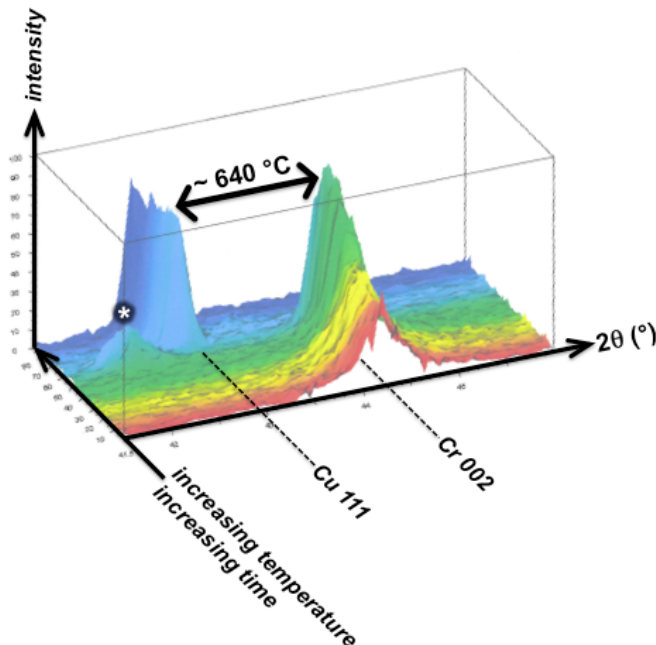


Figure 2: *In situ* X-ray diffraction scans as a function of increasing temperature for a nano-laminate being initiated thermally.

The electrical ignition via Joule heating of oxygen exchange reactions in Cr-CuO nano-laminates with a range of interface densities was also demonstrated. In these studies electrical leads were attached to two ends of a sample, and the voltage was increased until rapid initiation of the sample was achieved. Shown in Figure 3 are x-ray diffraction patterns for the three samples shown in Fig. 1 in the as-deposited state and after the application of 50 V to initiate oxygen exchange. S, M, and L correspond to samples with layer thickness that are small, medium, and large, or A, B, and C in Figure 1, respectively. The x-ray data shows that the extent of reaction increases as the interface layer density increases, which suggests that ignition rate and thus power output can be controlled by the layering geometry.

TEM analysis was used to compare microstructures of a Cr-CuO nano-laminate where the oxygen exchange was initiated by voltage (Joule heating) and conventional thermal annealing. Shown in Figure 4 are cross section images pre- and post-ignition of a nano-laminate containing 19 layers. Panel B corresponds to the as-deposited state, panel A is after electrical ignition, and panel C is after thermal

ignition. For thermal ignition, where x-ray diffraction analysis indicates that the reaction occurs over several minutes, a structure that remains intact is observed that consists of continuous  $\text{Cr}_2\text{O}_3$  and Cu layers. In (A) a disrupted structure with minimal memory of the parent multi-layers and large voids are observed. Regions adjacent to the voids appear glassy in nature with evidence of melting. These are extremely refractory phases suggesting that temperatures in excess of  $2000^\circ\text{C}$  were achieved during the reaction process.

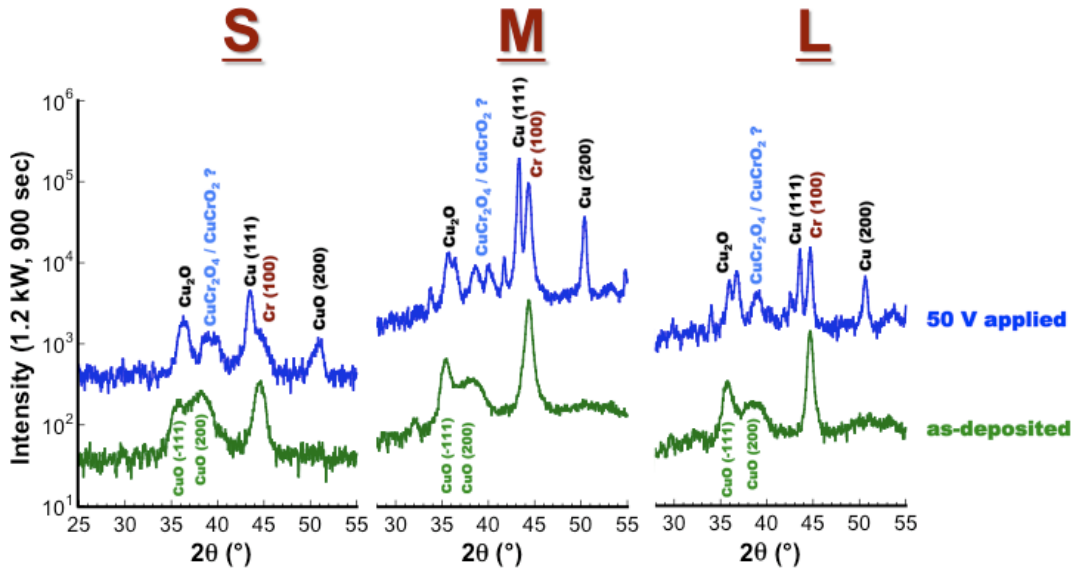


Figure 3: X-ray diffraction patterns for the three samples shown in Fig. 1 in the as-deposited state and after the application of 50 V to initiate oxygen exchange. S, M, and L correspond to samples with layer thickness that are small medium and large, or A, B, and C in Figure 1, respectively.

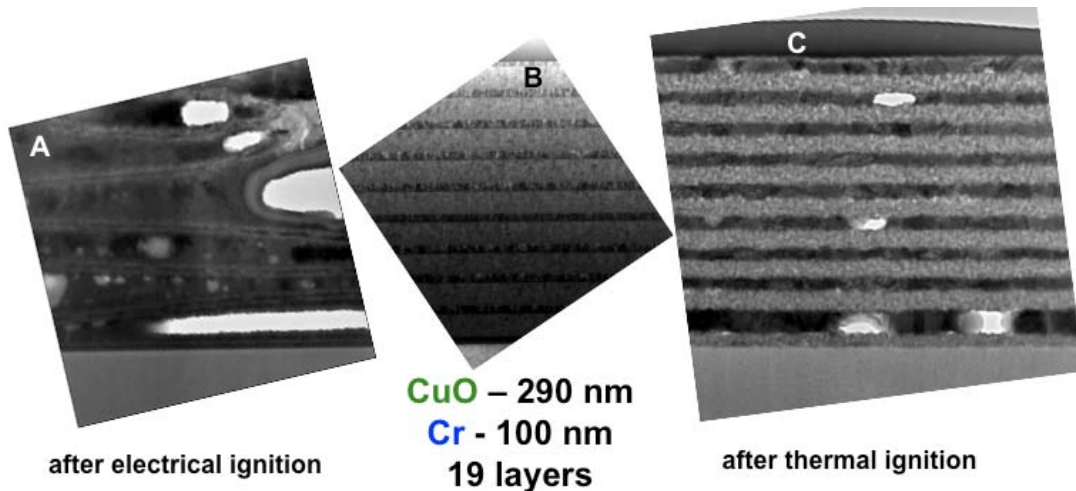


Figure 4: Cross sectional TEM images before (panel B) and after initiation by electrical (panel A) and thermal means (panel C).

## IV.2 Simulation Effort

The methodology used in our modeling effort was developed in the Brenner and Irving research groups.<sup>6</sup> Two concurrent simulations are carried out. One is a molecular dynamics simulation in which atom trajectories are followed by integrating classical equations of motion with inter-atomic forces derived from an analytic potential energy function. For the studies reported here a many-body embedded-atom method potential is used. Overlaid on the simulation is a static grid with the temperature and density profile of each grid region established to match that of the underlying atomic simulation. The second simulation solves the heat and electrical transport equations on this grid using virtual heat and current resistors that connect each grid region. An ad hoc feedback between two calculations is established through a specialized thermostat in the atomic simulations and by updating the density and temperature profile in the grid. Hence the approach adds to a continuum transport simulation associated atomic dynamics. In turn, proper Joule heating and heat transfer is incorporated into the atomic simulation without explicitly treating electronic degrees of freedom. Using these codes, we followed the dynamics of Al nanostructures within a Ni substrate subject to Joule heating as a function of voltage, initial structure, and the assumed relationship between resistivity and alloy composition. In addition, we were able to decouple the atomic and continuum simulations, and therefore examine the system temperature as a function of voltage without the exothermic chemistry associated with the mixing of Ni and Al.

Plotted in Figure 5 is the maximum temperature as a function of time for a 0.5 V applied voltage across a simulated system containing an Al cube embedded within a Ni substrate. The atomic region is in turn embedded within a continuum where just the heat and current transport equations are solved. The cross-sectional dimensions of the system are 17.6nm x 17.6 nm. The length of the atomistic region is 24.64 nm; the total length including the continuum is 122.5nm. The solid line corresponds to Joule heating with no chemical dynamics; the dashed line is from the multi-scale modeling that includes atomic dynamics. The melting voltages for Al and Ni are indicated by the horizontal lines. With only Joule heating the system does not reach a sufficiently high temperature to melt the nickel, and the rate of mixing and resulting energy release is limited by the dissolution solid Ni into molten Al. With heating from chemical mixing included, the system heats to above the Ni melting point, which accelerates the temperature rise due to the faster liquid-liquid mixing compared to the solid-liquid mixing.

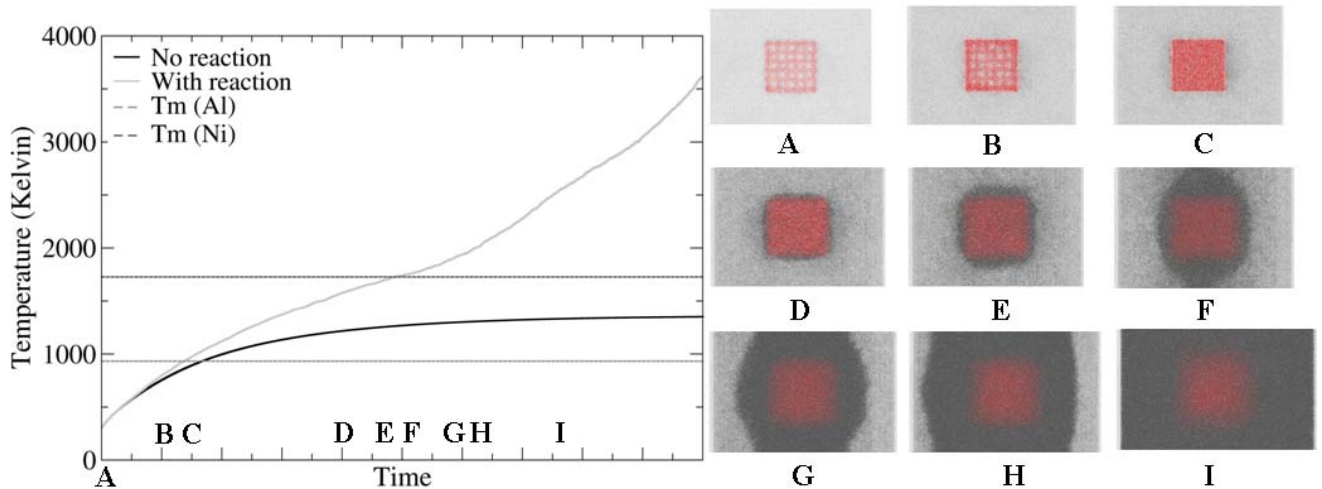


Figure 5: Temperature as a function of time and snapshots from the simulation for the simulated Joule heating of a Ni-Al nanostructured composite.

The lettered snapshots from the simulation illustrated at the right of the Figure 5 correspond to the letters on the time axis. Al atoms are red, Ni atoms are grey. The Al begins to melt at about frame C.



Interface disordering prior to Ni melting is apparent in frame D. The melting of the Ni that accelerates the temperature rise begins at the molten Al-Ni interface and grows into the surrounding Ni (frames E-I)

Additional data from the simulation described in Figure 5 is shown in Figure 6. The top plots are temperature as a function of position and time; the bottom plots are the change in temperature as a function of position and time. The left frames are for Joule heating only; right frames include atomic dynamics coupled to the continuum. For Joule heating only, the system reaches steady-state with temperature-position described by a parabola as expected. When chemical energy release is included, the temperature rise exceeds the Joule heating, and accelerates as the melting point of Ni is exceeded. In this case the heat release is very rapid and the system displays what appears to be thermal runaway.

One of the goals was to demonstrate how the nanostructure of the Ni-Al can be used to control the path that the current flows due to an applied voltage and, as a result, tune the local Joule heating to produce fine control of initiation. However, the simulations have shown that the resistivities of Ni and Al are too similar to significantly tune the energy release process via targeted Joule heating within the initial geometries; instead, slow energy release for Al melt + Ni solid versus faster energy release for Al melt + Ni melt dominated all geometries. These results, however, do not preclude the possibility that the voltage can be time varied to control initiation dynamics, and that this temporal variation can be coupled to the initial structure.

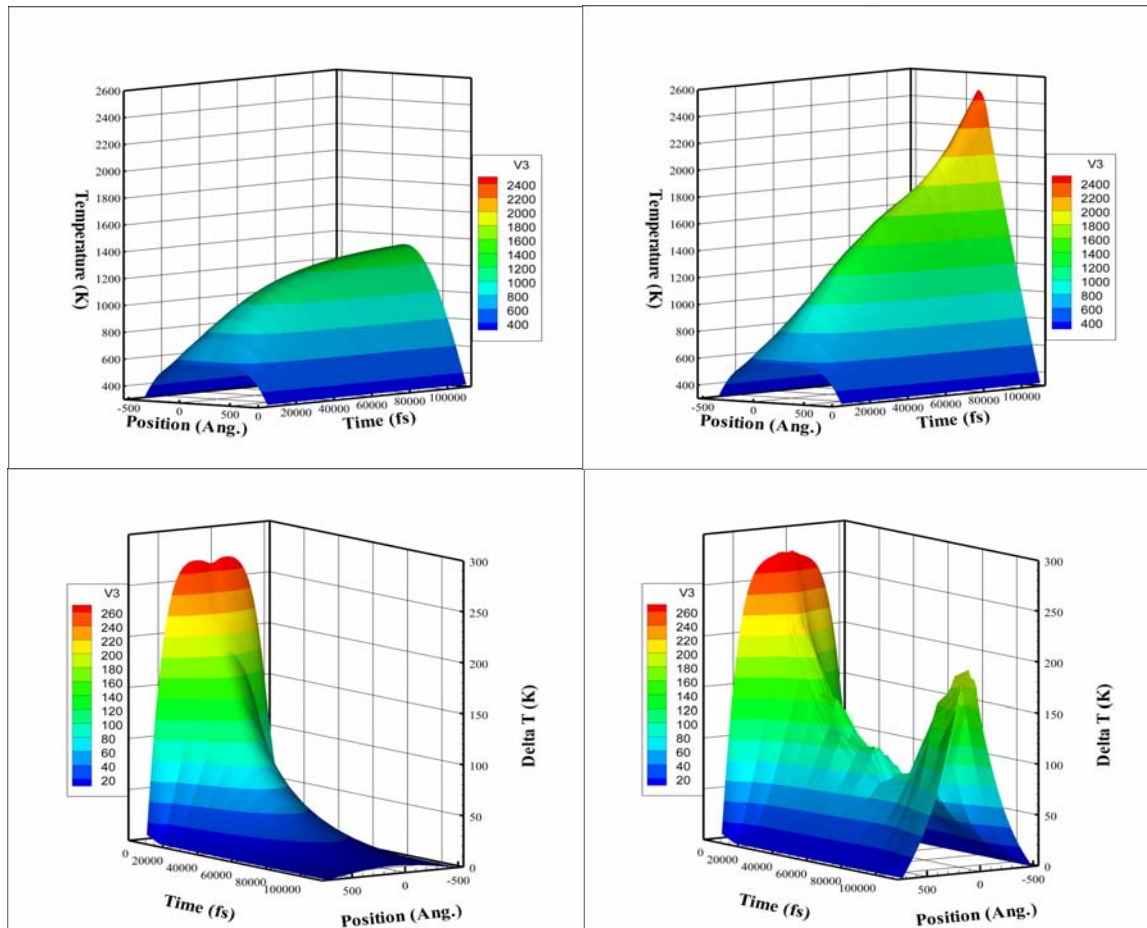


Figure 6: Additional data from the simulation described in Figure 5. Top plots are temperature as a function of position and time; bottom plots are change in temperature as a function of position and time. The left frames are for Joule heating only; right frames include atomic dynamics.

## V. Additional Research

The experimental effort has been successful in demonstrating that these nano-laminates can be engineered to precise dimensions, and that their properties can be well characterized with respect to thermal and electrical initiation. The modeling was also successful in demonstrating that initiation by Joule heating can be simulated with multi-scale modeling and that new insights can be developed from these simulations regarding the limitation of mass transport and melting dynamics on the control of power output. As an extension to this work, systematic analysis by experiment and modeling on how the oxide properties may effect oxygen rates and, hence, power output and initiation dynamics appears to be a promising basic science avenue with potential implications for energetic materials as both structures and initiators that predictably respond to heat, shock, and electrical stimuli.

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